29. Deutsche Zeolith-Tagung, 1. - 3. März 2017, Frankfurt am Main

Improving Electrocatalytic Performance of Noble-Metal-Free Catalysts by Ionic Liquid Modification

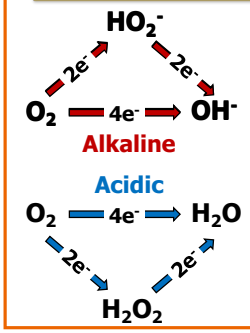
TECHNISCHE UNIVERSITÄT DARMSTADT

T. Wolker, G.-R. Zhang, N. Erini, U. Kramm, B.J.M. Etzold*

Introduction

Highly active oxygen reduction reaction (ORR) electrocatalysts that are stable under operating conditions are needed in order to enable a widespread commercialization of polymer electrolyte membrane fuel cells (PEMFCs). State-of-the-art ORR catalysts are mostly based on platinum. Due to their high price noble-metal-free alternatives are highly desirable [1]. Carbon-based materials emerge as one of the promising candidates due to their remarkable advantages of low cost, abundant structural variety, tailorable surface chemistry, and good conductivity. Tremendous efforts have been made to improve the performance of carbon-based materials for ORR, mainly through modifying the inherent structures of carbon by doping heteroatoms (e.g., B, N, P) or combining with metal/metal oxides. However, these systems often show a poor stability during electrochemical cycling and therefore still need to be improved in order to replace state-of-the-art noble metal catalysts. Quite recently we have demonstrated that filling the pores of Pt/C catalysts by a minor amount of Ionic Liquid ([BMIM][NTf_2], [MTBD][NTf_2]) would significantly boost the catalytic activity of Pt/C for ORR [2,3]. This was explained by the fact that the modification led to a new microenvironment around active centers that would prevent the poisoning with oxygenated species. Inspired by this work, herein we intend to transfer this strategy to the non-precious metal catalysts (NPMC, e.g., N-doped carbon black).

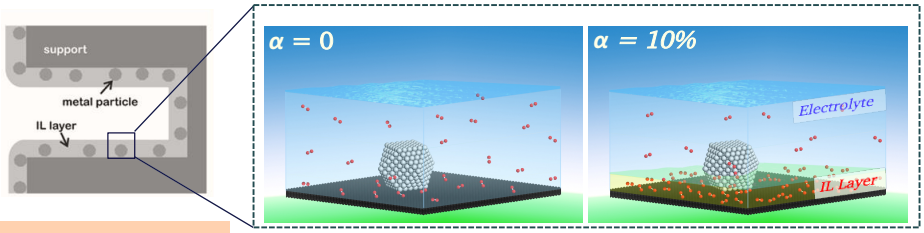
Oxygen Reduction Reaction



Highly active catalyst needed to overcome sluggish kinetics

Selectivity towards 4 e^- - pathway desired

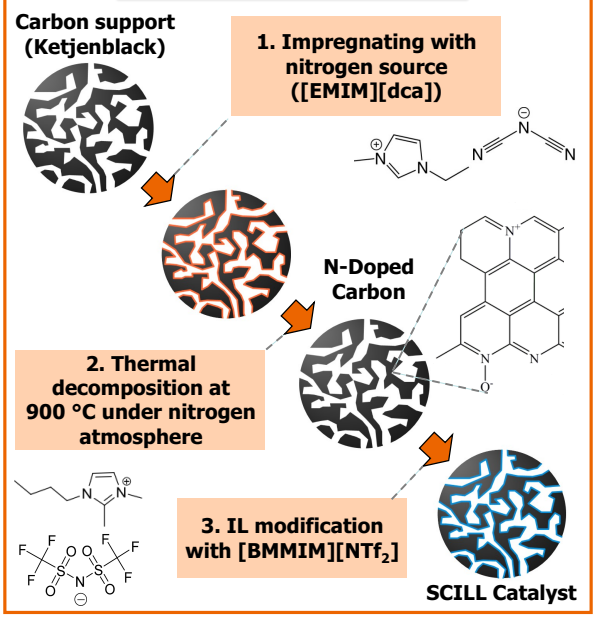
Solid Catalysts with Ionic Liquid Layer (SCILL concept)



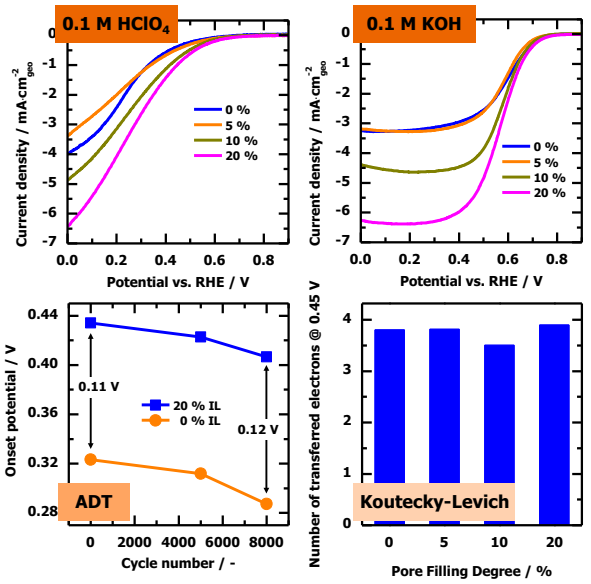
α: pore filling degree
$\alpha = V_{IL}/V_{pore,0}$

The pores of a catalyst are partially filled with Ionic Liquid to create a new microenvironment around active centers

Catalyst preparation



Nitrogen-doped carbon – SCILL: ORR performance



[BMMIM][NTf_2] can boost the activity of N-Doped carbon in acidic and alkaline media

The stability is also increased after IL-modification

The selectivity towards the 4 e^- pathway is not influenced by the IL-modification

Conclusions

- Nitrogen-doped carbon was prepared by thermal decomposition
- The pores of this catalyst have been partially filled with Ionic Liquid to form a SCILL catalyst
- By this IL modification the catalytic ORR activity was significantly boosted
- The boosting effect is highly sensitive to the pore filling degree of IL
- Durability tests revealed an increased stability after IL modification
- SCILL approach is a new perspective to high performance ORR catalysts

This project has received funding from the European Research Council (ERC) under the European Union's Horizon 2020 research and innovation programme (grant agreement n° 681719)

literature: [1] Y. Nie, L. Li, Z. Wei, *Chem. Soc. Rev.* 44 **(2015)**
[2] G.R. Zhang, M. Munoz, B.J.M. Etzold, *ACS Appl. Mater. Interfaces* 7 **(2015)**
[3] G.R. Zhang, M. Munoz, B.J.M. Etzold, *Angew. Chem. Int. Ed.* 55 **(2016)**